Investigation on the Relationship of the Relative Molecular Mass of Scale Inhibitor AA/MAC and the Synthesis Conditions

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***Abstract*: In this paper, it was investigated that the monomer ratio, the dosage of the initiator, reaction temperature and time influenced the molecular weight of synthetic products. The research showed that the molecular weight of scale inhibitor was increased with the different synthesis conditions, which were acrylic dosage, reaction temperature and time, but the molecular weight was decreased with increasing amount of the initiator. The experiment of resistance calcium scale indicates: the molecular weight is too high or too low, the effect of scale inhibition is not ideal.**

Keywords:* *copolymer, relative molecular mass, influencing factors, scale inhibition effect

Acrylic copolymer scale inhibitor is one of the efficient scale inhibitors universally used in oil-water wells and line pipes[1-7]. The effect of scale inhibition of this kind scale inhibitor relates to various factors in which relative molecular mass affects scale inhibition most[8-13]. The copolymer scale inhibitor presents different effects of scale inhibition along with different relative molecular mass, and relative molecular mass is related to monomer ratio, the dosage of the initiator, reaction temperature and time[14-16]. This paper aims at synthetic acrylic and methyl acrylic biopolymer scale inhibitor used in oilfield to explore how synthetic condition influences relative molecular mass and also the relation between synthetic condition and the effect of scale inhibition.

I. EXPERIMENTAL SECTION

A. Experimental Apparatus and Major Chemicals

JJ-1 multi-function agitator, CS501 super thermostatic water bath, dropping funnel, neck flask, Ubbelodhe viscosimeter, thermostatic water bath. Acrylic acid, methyl acrylate, sodium sulfite, ammonium persulfate and sodium chloride. They are all analytically pure.

B. Synthesis Experiment of AA/MAC Biopolymer

Adding quantitative dosage of acrylic acid/ methyl acrylate, sodium sulfite and distilled water into a neck flask with a moter agitator and a dropping funnel in it. Warming and stirring it to a certain temperature, then adding drops of left the mixture of acrylic acid and methyl acrylate and ammonium persulfate, during which process should pay attention to the dropping pace and keep the reaction temperature invariant, after the reaction for a while cooling and adjusting pH=7 to get the required copolymer scaled inhibitor AA/MAC.

C. Measurement of Viscosity Average Molecular Weight

Experiment principle: in the research of polymer, viscometry is usually employed to measure the viscosity average molecular weight, and it is often used to express the relative molecular mass. The apparatus of this method is easy, the operation is convenient, and it can get to the degree of precision required by the research. Viscosity method is based on the principle that the viscosity of linetype polymer solution increases along with the increase of molecular weight. Because of the complexity of molecular conformation of high polymer, the relation between viscosity and molecular weight is set up by empirical equation Mark-Houwink equation $[\eta] = K(\overline{M}_\eta)^\alpha$. The equation shows that viscosity

average molecular weight of polymer is only related to its intrinsic viscosity η, and K、α is constant in a certain region which can be looked up in a table. Therefore, it only needs to measure the intrinsic viscosity of scale inhibitor.

Experiment steps:

1) Intrinsic viscosity η measurement of acrylate copolymers

Intrinsic viscosity of acrylate copolymers is measured by five dilution method using Ubbelodhe viscosimeter.

2) Viscosity average molecular weight computation of acrylate copolymers

Based on Mark-Houwink equation $[\eta] = K(\overline{M}_\eta)^\alpha$, we can infer that the calculation method of viscosity average molecular weight is $\overline{M}_\eta = \left(\frac{[\eta]}{K}\right)^{\frac{1}{\alpha}}$, and the values of K and α could be consulted to the sodium polyacrylate parameter values which are K=15.47*10-3、α=0.9.

D. The Measurement of the Scale Inhibition Effects of Scale Hibitors with Different Molecular Weight

To explore the scale inhibition effects of biopolymer with different molecular weight, we should combine bipolymer with different molecular weight by changing conditions of monomer ratio, the dosage of the initiator, reaction temperature and time. Then we can investigate that molecular weights of synthetic products in different conditions affect scale inhibition effect. Here it mainly used scale inhibition rate to express the scale inhibition effect. The specific scale inhibition and its evaluation method please consult SY/T5673-93.

II. RESULTS AND DISCUSSION

A. Effect of Monomer Ratio on Molecular Weight

Under the condition of certain 10% initiator dosage, 60℃ of reaction temperature and 2h of reaction time, changing two monomer ratios to make ratios between acrylic acid and methyl acrylate are 4:1，5:1，6:1，7:1 and getting the measurement of the relation between viscosity average molecular weight and monomer ratio as the following picture 1.

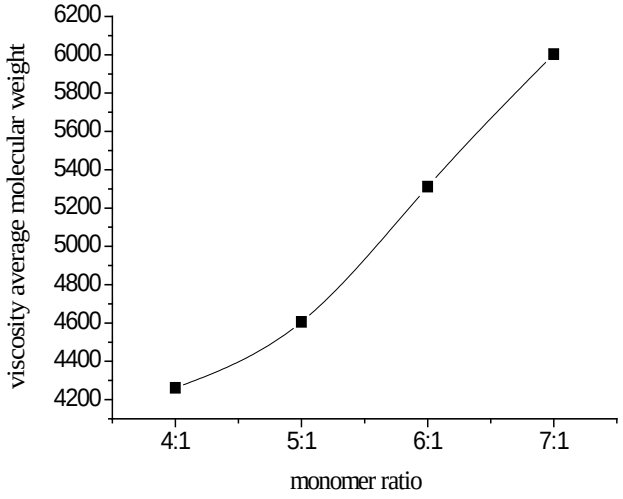

Fig. 1 Effect of Monomer Ratio on Molecular Weight

In picture 1, relative molecular weight of AA/MAC copolymer relates closely to monomer ratio, and its viscosity

average molecular weight gradually increases with the enlargement of monomer ratio. The reason is that along with the increase of monomer quantity of acrylic acid, the reactivity ratio increases and relative molecular mass of polymerizate is increasing constantly. [2]

B. Effect of Initiator's Dosage on Molecular Weight

Fixed monomer ratio 6:1, 60℃ of reaction temperature and 2h of reaction time, it studies the influences caused by the dosage of initiator to AA/MAC copolymer viscosity average molecular weight (as in picture 2).

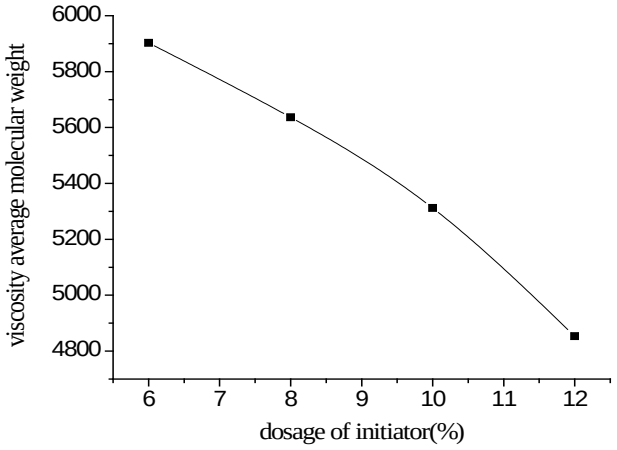

Fig.2 Effect of Initiator's Dosage on Molecular Weight

Picture 2 shows that with the other circumstances staying the same, increasing the dosage of initiator, viscosity average molecular weight of AA/MAC copolymer declines obviously. The reason is that along with the increase of the dosage of initiator, initiating rate increases, reaction tendency between molecules increases and reaction ratio gradually increases, therefore it causes the decline tendency of molecular weight.

C. Evaluation on Molecular Weight and Scale Inhibition Effected by the Changes of Reaction Temperature

Under the fixed condition of 6:1 of monomer ratio, 10% of the dosage of initiator, 2h of reaction time, only changing reaction temperature to measure the relation between reaction temperature and viscosity average molecular weight of polymerizate, as the following picture:

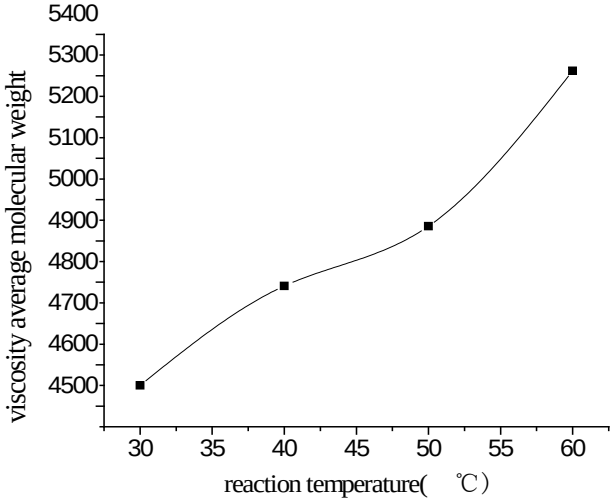

Fig. 3 Effect of Reaction Temperature on Molecular Weight

The result of picture 3 shows that with the other circumstances staying the same, the molecular weight of product goes up along with the increase of polymerization temperature. When the reaction temperature gets t℃,60 viscosity average molecular weight gets to the maximum of 5311. The reason is that the increase of temperature accelerates the formation of radical active monomer, and the increase of probability of collision among radicals helps to accelerate the reaction rate and increase the molecular weight.

D. Effect of Reaction Time on Molecular Weight

Under the fixed condition of 6:1 of monomer ratio, 10% of the dosage of initiator and 60℃ of reaction temperature, only changes the reaction time and gets the relation between reaction time and molecular weight, as the following picture:

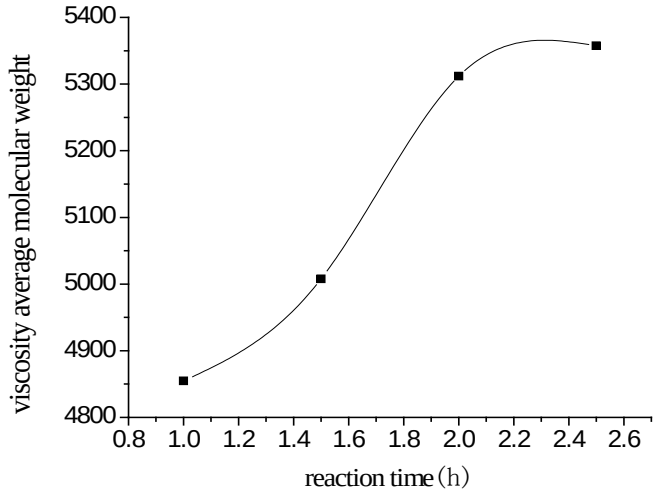

Fig.4 Effect of Reaction Time on Molecular Weight

The picture 4 shows that in the first 1-2 hours of reaction, molecular weight grows faster and later it grows slower, but it increases in general. The reason accounted for it is that along with the increasing time, degree of polymerization is increasing. In the beginning of reaction, density of both monomer and initiator is high, the percent conversion of monomer is rapid, and the increase of molecular weight is also fast; with the extending of time, monomer and initiator are gradually consumed, the percent conversion of monomer turns slowly, therefore molecular weight increases slowly until keeps stable.

E. Effect of AA/MAC Molecular Weight on Scale Inhibition

Based on the previous different conditions, for example, change of monomer ratio, initiator, temperature and time, polymerize AA/MAC biopolymer with different molecular weight then take a research on the effects of scale inhibition of different molecular weights. We have the results as in the Picture 5. The dosages of copolymer are all 40mg/L.

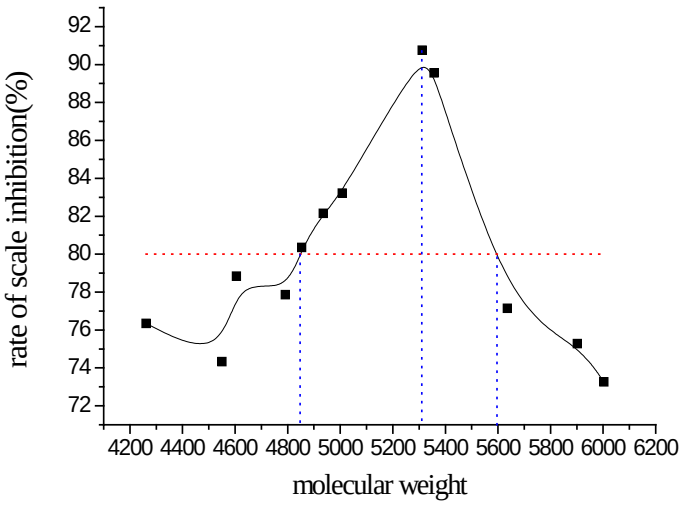

Fig.5 Effect of AA/MAC Molecular Weight on Scale Inhibition

From this picture, we can find out that there is a close relation between the effect of scale inhibition of synthetic product and the change of molecular weight. The tendency of the affects of molecular weight to the effect of scale inhibition goes up first and then goes down. When the molecular weight of product is relatively low, the effect of scale inhibition is not satisfied. Along with the increase of relative molecular mass, the stability of calcium ion increase, and the effect of scale inhibition also grows up. When the Molecular weight gets to 5311, the rate of scale inhibition gets to the maximum 90.75%. After that, with the increase of molecular weight, the rate of scale inhibition appears to decrease, especially when the molecular weight of copolymer scale inhibitor is over 6000, the rate of scale inhibition gets to the minimum. It is obvious that polymer needs a scope of appropriate relative molecular mass which should be neither too high nor too low.

III. CONCLUSION

1） With the other factors keeping the same, it is not hard to find out that with monomer ratio, reaction temperature and reaction time increasing in a certain range, molecular weight of product has a tendency of rise. However, increasing the dosage of initiator in a certain range, leads the molecular weight of polymer declines.

2） After testing scale inhibition of polymer with different molecular weights, it is reasonable to draw a conclusion that polymer needs a proper scope of relative molecular mass and it is not good to the effect of scale inhibition if the relative molecular mass is too high or too low.

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